Characterization of Spherical Alumina Particles Obtained by Melting in a Hydrogen-oxygen Flame

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Spherical oxide particles can be used as mineral fillers, paint pigments, polishing materials and catalysts. They can be prepared using various techniques involving precipitation and spray drying. Melting of particles in a high-temperature flame is a simple technique which produces particles with a high degree of sphericity and high smoothness from non-spherical feed material. In current research the preparation of alumina particles by melting the feed material in a hydrogen-oxygen flame is described. The spherical particles obtained were characterized using scanning electron microscopy, atomic force microscopy, energy dispersive spectroscopy, X-ray diffraction, Fourier transform infrared spectroscopy and electrokinetic measurements. The particles prepared exhibit a high degree of sphericity and a low level of roughness. The chemical composition of the material after preparation is unchanged, however the crystallographic structure is different. It is suggested that alumina changes from pure α-alumina to a mixture of different transitional forms. Changes in the electrokinetic behavior were also observed for alumina which can be attributed to the strong dehydration of the oxide surface and/or change in the crystallographic structure. Also, the possible accommodation of trace amount of impurities in the surface zone during melting cannot be ignored.

INTRODUCTION

Inorganic spherical particles have important technological applications which are related to their well defined and smooth surface, good packing and good rheological properties. Spherical inorganic particles can be obtained using several different methods, including

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precipitation from solution (Matijevic and Wilhelmy 1982; Blendell, Bowen, and Coble 1984; Williams, Yocom, and Stofko 1985), ultrasonic spray pyrolysis (Milosevic, Jordovic, and Uskokovic 1994), and melting in a flame (Chen, Gleiman, and Phillips 2001).

Alumina particles are of considerable importance because of their wide use in many applications including use as polishing medium or filler material. It has been found that application of spherical alumina particles instead of irregular ones greatly improves the performance of chemical-mechanical polishing (Basim et al. 2000, 2001), the properties of polymer-filler blends (Chiba, Takahashi, and Otaguro 1988), and the surface properties of magnetic data storage media (Trippel et al. 1988). Spherical alumina particles are also used for the formulation of advanced ceramic materials (Noma et al. 1993; Lopez-Navarrete and Ocana 2001) and even in cosmetics (Tanaka and Miyasaki 1998).

Spherical alumina particles can be obtained using several methods. Hydrolysis of aluminum compounds (Catone and Matijevic 1974; Nishikawa and Matijevic 1994), sol-gel synthesis (Chatterjee et al. 2000), and spray pyrolysis (Murugavel et al. 1998) are the most common. Fused spherical alumina particles can also be obtained by melting non-spherical feed material in a high-temperature plasma flame (Hamano and Asaga 1974; Chen, Gleiman, and Phillips 2001) or by combustion of elemental aluminum particles (Abe, Ogawa, and Kondo 1998). These high temperature processes are especially convenient because they allow a cheap, non-spherical feed material to be transformed into the fused spherical alumina particles of high sphericity and smoothness.

In this paper we describe a relatively simple laboratory setup for the preparation of spherical particles by melting non-spherical material in a hydrogen-oxygen flame. The procedure can be used for preparation of different inorganic spherical particles, especially oxides. This setup was used to transform non-spherical polishing α-alumina into a spherical alumina particles. Feed material and the prepared spherical particles were characterized in detail, with respect to shape, surface morphology, elemental composition, crystallographic structure, and electrokinetic behavior of particles.

EXPERIMENTAL

Materials

Buehler 5 μm polishing alumina (Buehler Ltd.) was used in the experiments. High purity hydrogen and oxygen (Mountain Airgas) were used to create the flame for the preparation of spherical particles. Reagent grade KCl, HCl and KOH (Mallinckrodt) were used for electrokinetic measurements. All solutions were prepared using water deionized and purified using Milli-Q system (Millipore).

Methods

Preparation of Spherical Particles. Spherical alumina particles were manufactured using the laboratory setup shown on Figure 1. Raw alumina particles (feed material) were placed in a gas-washing bottle and oxygen from a cylinder was passed through the alumina bed at a rate to maintain the bed in a fluidized state. The washing bottle was placed in the ultrasound bath in order to prevent clogging of the tube delivering oxygen and to prevent channel formation in the particle bed. The oxygen stream, containing suspended alumina particles, was subsequently directed to the laboratory concentric gas torch where it was mixed with hydrogen. The hydrogen-oxygen flame reaches a temperature of 2700 °C which is sufficient to melt alumina particles (m.p. 2053 °C). The hydrogen-oxygen flame was directed into an 0.6 m quartz tube, the conical end of which

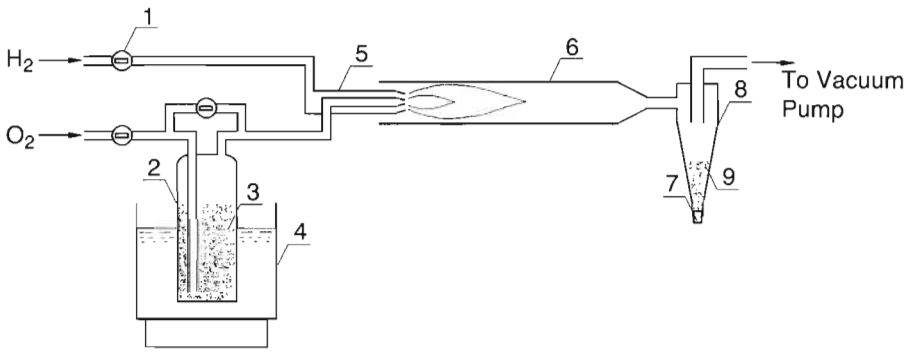

FIGURE 1 Schematic of the laboratory setup for preparation of spherical alumina particles: (1) valve, (2) washer bottle, (3) feed material, (4) ultrasound bath, (5) concentric torch, (6) quartz tube, (7) stopper, (8) cyclone, (9) collected spherical particle

was connected to a small glass cyclone (2 cm diameter). The outlet of the cyclone was connected to a pump which provided sufficient suction for pneumatic transport. Alumina particles, molten in the flame, were carried with the gas stream to the cyclone, undergoing cooling and solidification during transport. The spherical alumina particles were separated from the gas stream in the cyclone due to the centrifugal force and were collected at the bottom of the cyclone. The prepared spherical particles were removed from the cyclone through the port at the bottom.

Scanning Electron Microscopy (SEM). Alumina particles were mounted on a carbon tape and covered with a 20 nm thick gold layer using a Cressington Sputter 108 Auto Coater. Images of the particles were taken by means of Hitachi S-3000N SEM, using a secondary electron detector at a working distance 14.5 mm and 20.0 kV of electron energy.

X-ray Diffraction (XRD). The X-ray diffraction analysis was performed using Rigaku D/MAX x-ray diffractometer. The following scan parameters were used during measurements: step size 0.02°, scan speed 1 deg/min, slit width 1 mm, scatter 1.0°, receiving 0.15 mm. The alumina particles were analyzed as received. They were not grounded for the experiment and their size of approximately 5 μm was found to be sufficient to obtain good quality spectra.

Energy Dispersive Spectroscopy (EDS). The SEM-EDS (Energy Dispersive Spectroscopy) analysis was performed using a Hitachi S-3000N SEM instrument with EDS detector manufactured by EDAX, Inc. and using EDAX SEM Quant ZAF software. The spectra were obtained at a working distance of 14.5 mm working distance and 20.0 kV accelerating voltage. The alumina particles were deposited on the conductive carbon tape prior to the analysis. Spectral information was collected from 150 × 150 μm area covered with particles.

Atomic Force Microscopy Imaging (AFM). The surface of the spherical particles was examined using the Digital Instruments Nanoscope IIIa AFM. Measurements were done in the contact mode (in air) and a triangular silicon nitride cantilever (Digital Instruments, Inc.—spring constant 0.12 N/m) was used.

Electrokinetic Measurements. Electrophoretic mobility of the alumina particles was measured using the Brookhaven ZetaPALS apparatus (McNeil-Watson, Tscharnuter, and Miller 1998). The measurements were taken after 120 h of equilibration in 1×10^{-3} M KCl solution. Prior to measurement the pH was adjusted using solutions of HCl and KOH.

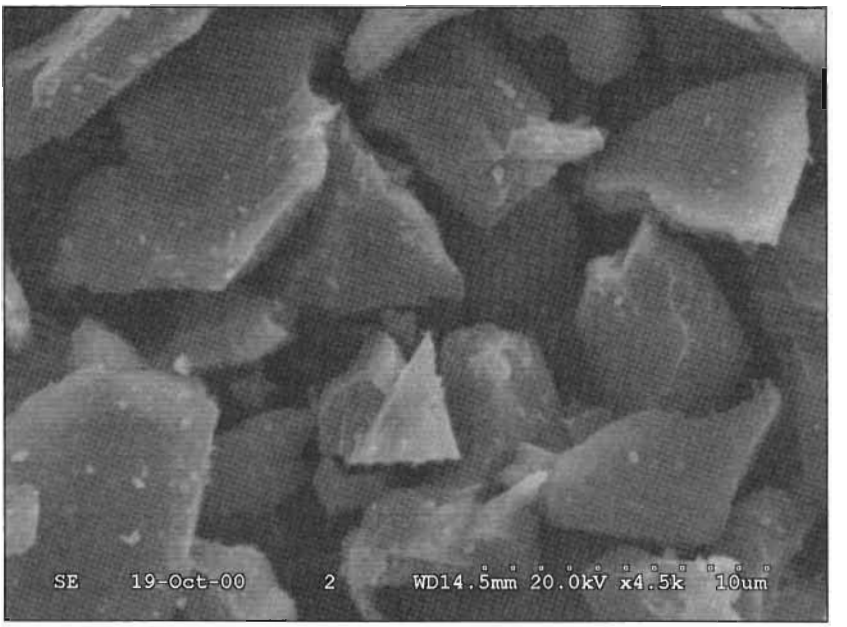

FIGURE 2 SEM image of feed alumina particles

Six consecutive measurements were taken at room temperature and the measurements were averaged and the zeta potential was calculated using the Smoluchowski equation.

RESULTS AND DISCUSSION

Particles of the feed material are shown in the SEM micrograph, see Figure 2. Irregular particles with sharp edges with a size from 5 to 10 μm can be seen. The shape of these particles is typical for fractured material.

Elemental analysis done by EDS shows that except for the main compound, aluminum oxide, only small amounts of impurities are present as can be seen from Figure 3. The quantification of the elements present in the feed material is given in Table 1. Titanium, silicon, and magnesium are the most important impurities which have been found in this sample. The determination of chemical compounds in which these elements are present is impossible using EDS. It can, however, be assumed that they are mostly in the form of oxides, since no other elements were found in sufficient amount. It should be noticed that these impurities are evenly distributed in the feed particles. Scan of a large area was compared with EDS analysis for a single particle and no significant difference was found. Although during analysis several single particles were found to be more contaminated than others, the effect of these impurities on the overall population is negligible.

The X-ray diffraction spectrum, shown in Figure 4, demonstrates that the feed alumina is highly crystalline. The data when fitted to the literature values show a perfect match for the most stable form of aluminum oxide-α-alumina (corundum).

After passing through the hydrogen-oxygen flame in the apparatus schematically shown on Figure 1, feed material particles undergo drastic changes. The temperature of the flame is significantly higher than the melting point of alumina. After melting, the surface tension of molten alumina causes alumina droplets to form the most energetically

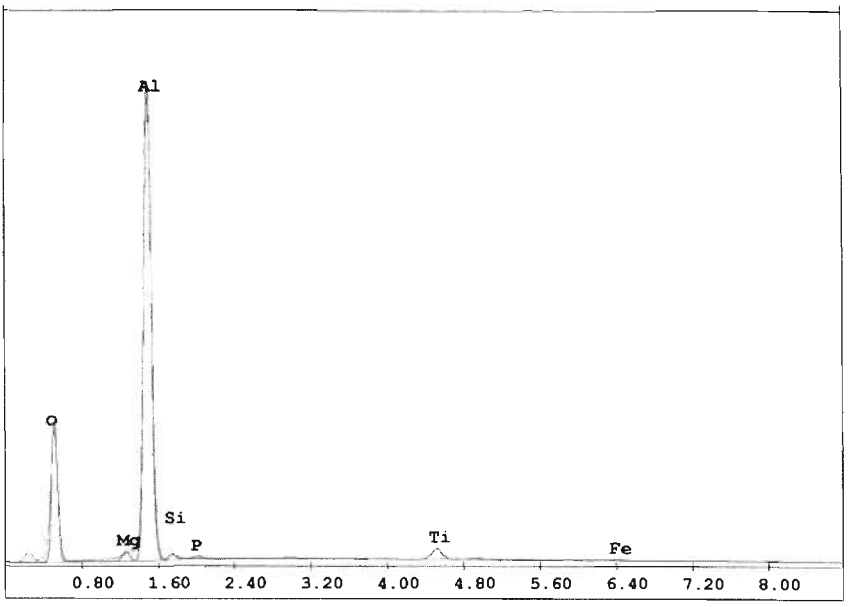

FIGURE 3 EDS spectrum of feed alumina particles

TABLE 1 Composition of feed alumina and spherical alumina particles

Element	Feed Alumina Particles (wt%)	Spherical Alumina Particles (wt%)
Al	54.16	54.10
O	39.25	40.25
Ti	3.17	2.93
Si	1.25	1.25
Mg	1.15	0.82
P	0.53	0.14
Fe	0.50	0.51

favorable spherical shape. An SEM image of these spherical alumina particles is presented in Figure 5. These particles are highly spherical and range in diameter from 2 to 5 μm. It can be deduced from the SEM image that the particles size is directly related to the size of the particles in the feed material. The probability of coalescence of two or more droplets of molten alumina in the flame must be extremely low at the small concentrations of particles in the gas stream. The breakage of the molten drop of alumina into smaller droplets due to the forces in the flame and/or gas stream is also difficult to imagine due to the high values of surface tension and viscosity of molten alumina.

Despite the high sphericity of the alumina particles, AFM analysis reveals that the surface of the particles is not completely smooth. Figure 6 shows a region of the surface for one of the larger spheres. The presence of ripples or terraces can be clearly seen. These terraces are on the order of 500 nm and more in size, while their height is usually around 40 nm. This geometry on the surface results in a mean roughness equal to 21 nm for the 5 × 5 μm scan. The origin of these features at the surface is not completely clear at

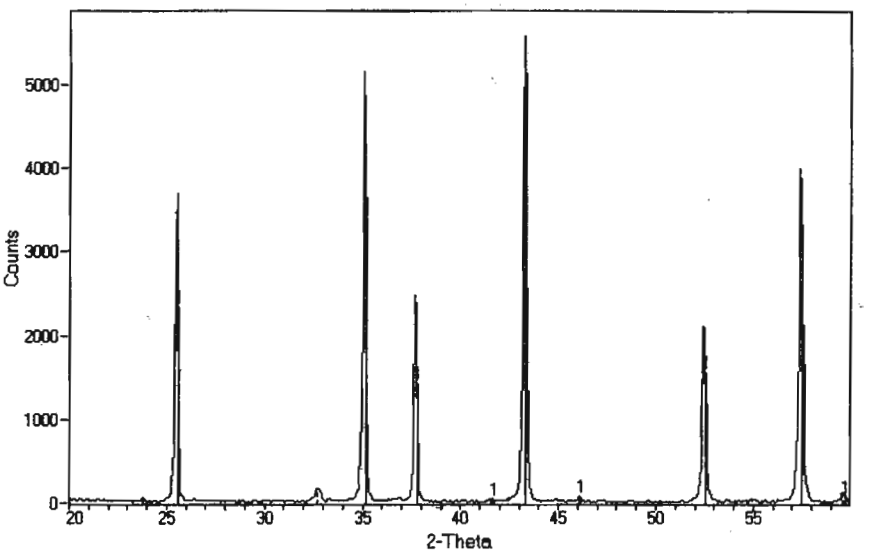

FIGURE 4 XRD spectrum of feed alumina particles

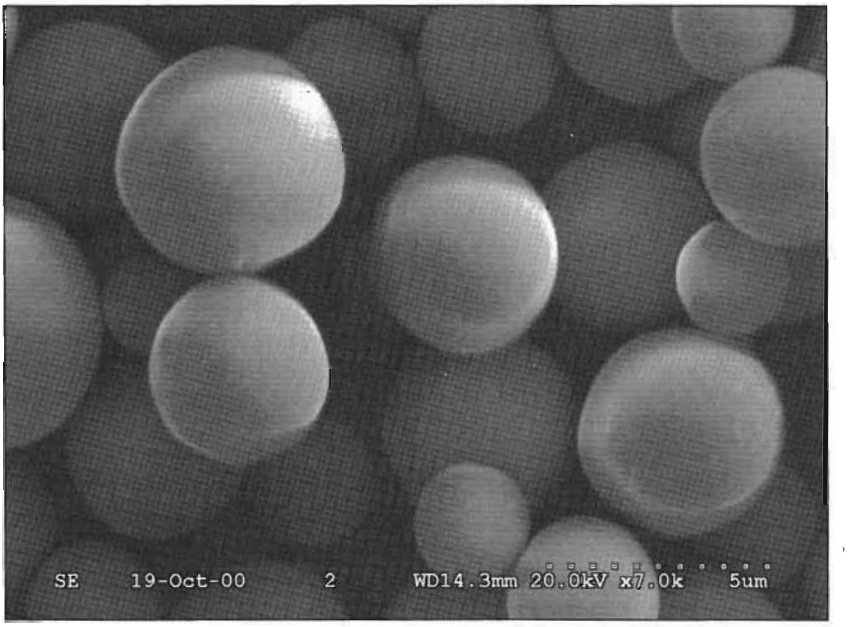

FIGURE 5 SEM image of spherical alumina particles

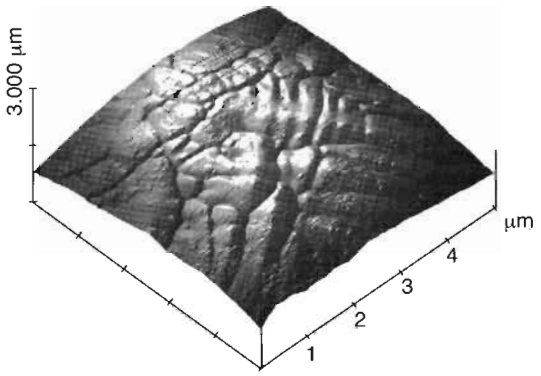

FIGURE 6 AFM image of the surface of a spherical alumina particle. Mean roughness for 5 x 5 µm scan is 21 nm.

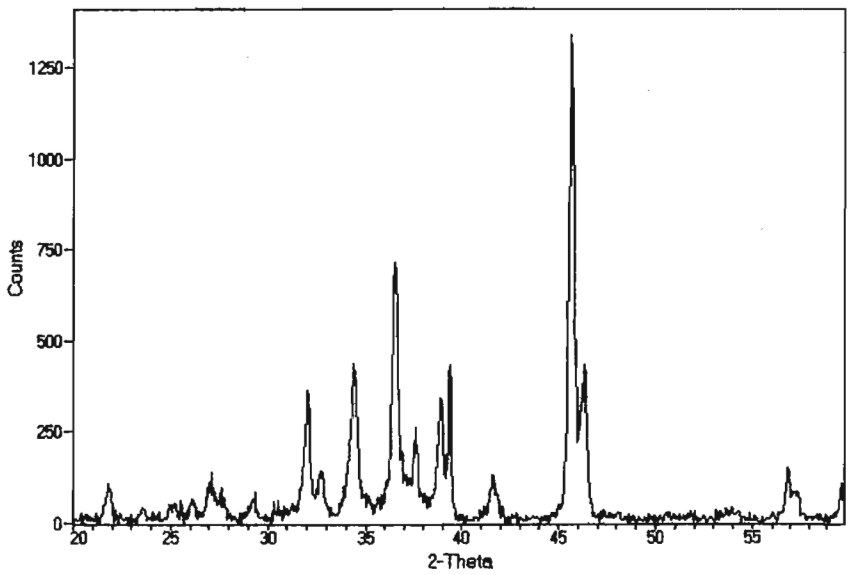

FIGURE 7 XRD spectrum of spherical alumina particles

this point. It could be the effect of quenching in turbulent flow, but also formation of crystallites at the surface cannot be ruled out.

EDS analysis of the spherical particles shows no significant difference when compared with the raw feed material spectrum, see Table 1. The results confirm the previous assumption that impurities are in the high-temperature resistant form, most probably oxides. It can also be concluded that no significant chemical changes are introduced (e.g., reduction) during the preparation of alumina spheres.

Despite almost the same chemical composition of the spherical particles and feed material, XRD spectra shows a huge difference between these two materials, as can be seen from comparing the spectrum in Figure 4 with that in Figure 7. The spectrum in

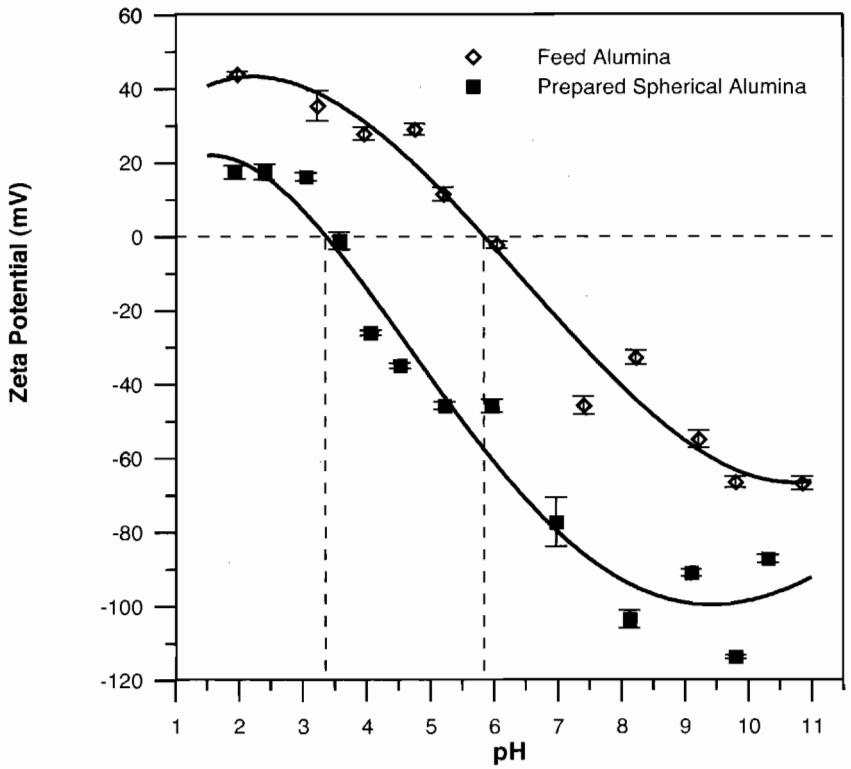

FIGURE 8 Zeta potential as a function of pH for feed material and spherical particles. IEP for feed alumina of irregular shape (feed material) is 5.8, for spherical particles is 3.4

Figure 7 shows that the spherical particles exhibit a high degree of crystallinity, however the diffraction pattern is very different from that of the feed material. It is known that alumina can be present in one of as many as 15 forms, where four of them are the most important: γ, δ, θ, and α. The α-alumina is thermodynamically stable form, while γ, δ, and θ are transitional forms during the transformation from hydrated alumina (boehmite) to the α-alumina (Santos, Santos, and Toledo 2000). These crystallographic forms change with an increase in temperature from the γ-alumina, through the δ, θ, and finally to the stable α-alumina form. However, the XRD spectrum for the spherical alumina particles cannot be fitted exactly to any one of these major phases. Judging from the spectrum shape these spherical particles might be a mixture of different phases, where δ-alumina and θ-alumina may be the predominant forms. Although the feed material is a stable α-alumina form, it is possible that during rapid quenching of molten alumina different, transitional phases can be formed. The presence of δ-alumina in spherical alumina particles has already been reported in the literature (Hiragushi et al. 1982).

The zeta potential of raw feed alumina and spherical alumina as a function of pH is shown on Figure 8. A long equilibration time (120 hours) was used in order to ensure complete hydration of the alumina surface. It was noticed that the surface does not reach the equilibrium and the zeta potential changes slightly even during first two to three days. The isoelectric point (IEP) of raw material was found to be approximately 5.8. Although this is a lower value than usually anticipated, it has to be noted that values reported in the

literature are in the range between 6.6 and 9.4. The degree of hydration and the presence of small amounts of impurities may significantly alter the electrokinetic behavior of particles. Surprisingly, after preparation and hydration, the spherical alumina particles became more negatively charged and their IEP shifted to a value of 3.4. Currently we are not sure if this effect is related to the differences between crystallographic structure of the feed and spherical product, differences in the hydration of these two samples or accumulation of impurities at the surface of sphere during the melting process.

CONCLUSIONS

The spherical particles of high-melting point oxides can be successfully prepared in the laboratory using a simple experimental setup. Particles obtained in a hydrogen-oxygen flame from non-spherical feed are highly spherical and relatively smooth. It was found that this process does not change the elemental composition of the particles significantly. A high degree of crystallinity was retained in the particles but the crystallographic forms changed from α-alumina to a mixture of transitional phases (most probably δ-alumina and θ-alumina). The change of IEP to a lower pH value (pH 3.4) after the treatment is not easy to explain without speculation and requires further studies on the influence of small amount of impurities in the alumina matrix and the effect of crystal structure on electrokinetic behavior.

ACKNOWLEDGMENTS

Financial support provided by the Department of Energy, Basic Science Division Grant No. DE-FG-03-93ER14315 is gratefully acknowledged. Although the research described in this article has been funded partially by DoE, it has not been subjected to the agency's required peer and policy review and therefore does not necessarily reflect the views of these agencies and no official endorsement should be inferred.

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